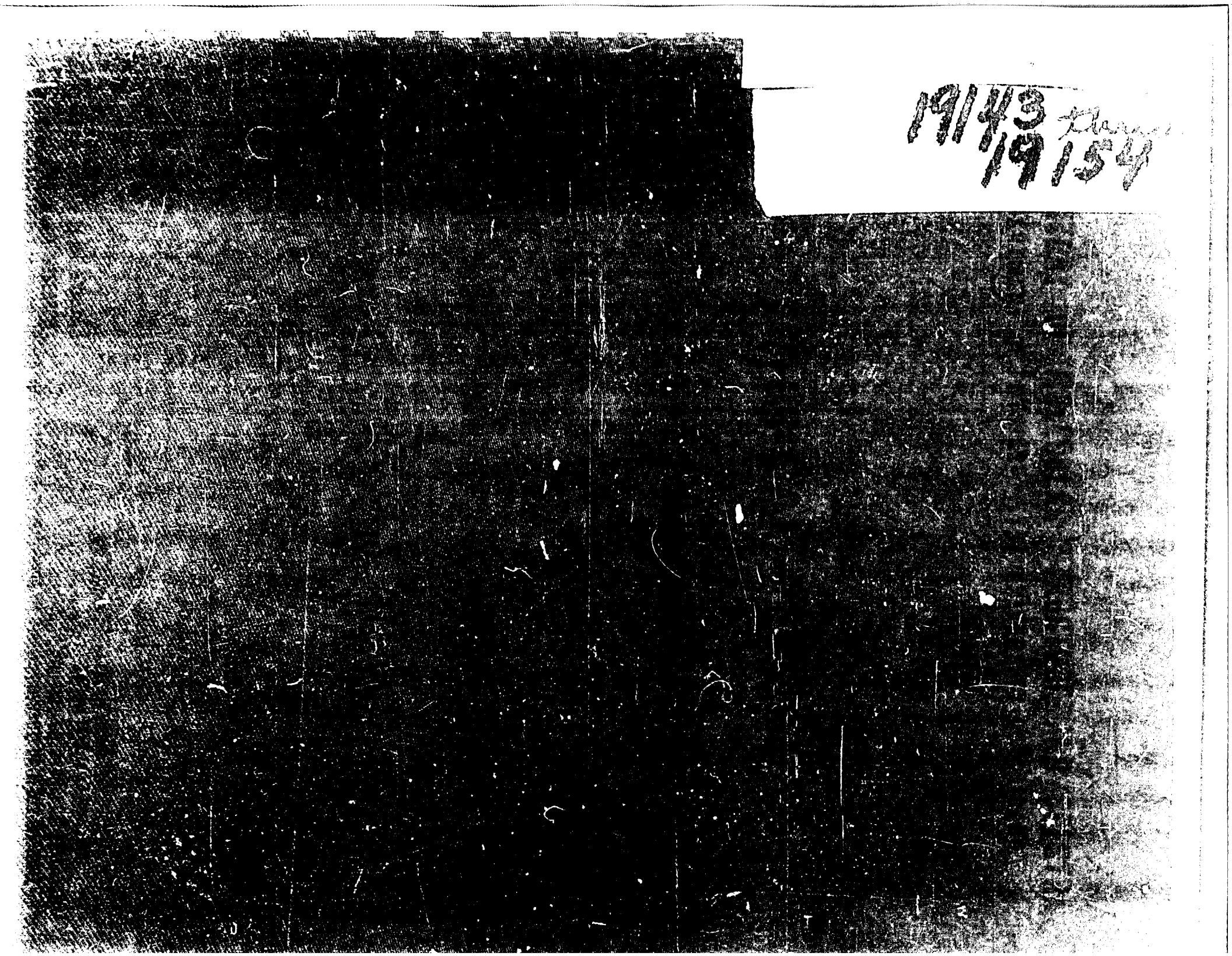
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LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA

DEPARTMENT OF PHYSICS • THE UNIVERSITY OF CHICAGO

TECHNICAL REPORT

1952 - 1953

PART ONE

For the period
1 April 1952 to 31 March 1953:
OFFICE OF NAVAL RESEARCH
CONTRACT N6ORI-20, TASK ORDER IX
PROJECT NR 019 101

For the period
24 June 1952 to 23 June 1953:
OFFICE OF ORDNANCE RESEARCH
CONTRACT DA-11-022-ORD-1002
PROJECT TB2-0001 (505)

PERSONNEL

Faculty

†‡*Professor R. S. Mulliken, Director°#
‡Professor W. G. Brown, Associate Deputy Director (from 16 September 1952)#
†‡*Associate Professor J. R. Platt°
*Assistant Professor C. C. J. Roothaan, Associate Deputy Director#
Visiting Associate Professor C. Reid (from 9 December 1952)

Research Associates

†*Dr. K. Ruedenberg
†‡Dr. Y. Tanaka (to 31 August 1952)
‡Dr. F. G. Wilkinson (from 1 September 1952)

Student Assistants

†Mr. R. A. Bonic (from 8 October 1952 to 17 April 1953)
†‡Mr. Charles E. Cohn (to 30 September 1952)
‡Mr. Paul W. Engler (from 23 March 1953)
†Mr. David M. G. Lawrey (to 15 June 1952)
‡Mr. Paul A. Michael (17 October 1952 to 23 February 1953)
†‡Mr. Morton Schagrin (to 10 August 1952)
†Mr. Charles W. Scherr (from 1 December 1952)

Computation Staff

†*Mr. Walter Jaunzemis
†Mr. Tracy J. Kinyon
*Mrs. Gudrun Lenkersdorf (from 22 June 1953)
*Mr. Philip I. Merryman, Jr. (from 21 October 1952)

Secretarial Staff

†‡*Mr. H. H. Brimmer, II, Secretary
†‡*Mrs. Eugenia Y. K. Bautista (from 23 September 1952)
†‡*Mr. William A. Lester, Jr. (from 30 April 1953)
†‡*Miss Arline T. Johnson (from 16 June 1952 to 5 January 1953)
†‡*Mr. Joel T. Rosenthal (from 6 January 1953 to 17 April 1953)

Associated Scientific Personnel

Mr. James E. Faulkner (to April 1953)
Mr. Joe S. Ham, Jr., AEC Predoctoral Fellow, 1951-53
Mr. Norman S. Ham, CSIRO Predoctoral Fellow, 1952-54 (from September 1952)
Mr. William L. Lichten, AEC Predoctoral Fellow, 1951-53 (from January 1953)
Dr. Harden M. McConnell, NRC Postdoctoral Fellow, 1950-52 (to May 1952)
Mr. A. D. McLean, Australian Canteen Fellow, 1952-55 (from September 1952)
Dr. W. J. Potts, Jr., AEC Predoctoral Fellow, 1950-52 (to December 1952)
Dr. A. V. Stuart, Shell Development Company (from September to October 1952)

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†Normally engaged under or associated with Office of Naval Research contract.

‡Normally engaged under or associated with Office of Ordnance Research contract.

*Normally engaged under or associated with Office of Scientific Research (Air Research and Development Command) contract.

°On leave of absence for the academic year 1952-53. Professor Mulliken is for the most part at Oxford University, England, under a Fulbright Award. Professor Platt is at King's College, University of London, and other scientific centers in Europe under a Guggenheim Memorial Foundation Grant.

#During Professor's Mulliken absence Professor W. G. Brown of the Department of Chemistry is Deputy Director for the research contract with OOR, and Professor C. C. J. Roothaan is Deputy Director for those with ONR and OSR (ARDC).

*On leave of absence from the Department of Chemistry, University of British Columbia.

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†Work assisted by the Office of Naval Research under Task Order IX of Contract N6ori-20 with The University of Chicago.

*Work assisted by the Office of Ordnance Research under Project TB2-0001 (505) of Contract DA-11-022-ORD-1002 with The University of Chicago.

FOREWORD

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1. Preface

Six previous comprehensive TECHNICAL REPORTS have been issued under Contract N6ori-20, Task Order IX, Project 019 101, with the Office of Naval Research: A Quarterly Report for the period 1 June 1947 to 31 August 1947; an Annual Report (in two parts) for the period from 1 September 1947 to 31 August 1948; a Report (in two parts) for the period 1 September 1948 to 31 March 1950; a Report (in two parts) for the period 1 April 1950 to 31 March 1951; and a Report (in two parts) for the period 1 April 1951 to 31 March 1952.

The present Report is being issued in an as yet undetermined number of parts. The Report is being published jointly under this Laboratory's contract with the Office of Naval Research as well as under Contract Number DA-11-022-ORD-1002, ORD Project Number TB2-0001 (505), with the Office of Ordnance Research. The Report as a whole will cover roughly the period 1 April 1952 to 31 March 1953 for the contract with the Office of Naval Research, and the period 24 June 1952 to 23 June 1953 for the contract with the Office of Ordnance Research.

This Part One of the present Report contains complete texts of finished articles recently published, now in press, or shortly to go to press, covering research partly or wholly supported by one or both of the two contracts. This foreword contains a notice about the reorganization of the TECHNICAL REPORTS of this Laboratory, a survey of the equipment and apparatus on hand and in use, a summary of the scientific papers in this Part One, and brief descriptions of work in progress in the Laboratory and of activities associated with the Laboratory.

2. Reorganization of TECHNICAL REPORTS

Beginning with the present Report, TECHNICAL REPORTS issued by this Laboratory will be changed in several respects. As already mentioned, such Reports will for some time be issued jointly under several research contracts (in the present Report for 1952-53, there are two such contracts concerned: one with the Office of Naval Research, the other with the Office of Ordnance Research). Each scientific paper in the Report carries an accreditation of the source of support for the research represented by the paper; in addition, the Table of Contents likewise indicates the source of support.

Under present plans, TECHNICAL REPORTS will be issued in several parts for each year--the number of such parts being determined largely by the bulk of the scientific papers on hand and the timeliness of issue. Each part will however be a self-contained unit, with appropriate summaries of the papers included therein, of work in progress at the time of issue, and of associated activities.

The present volume is the first to be issued under a new method of publication. For some time it had been hoped that some more satisfactory means of publishing TECHNICAL REPORTS for the various work carried on in the Laboratory than that employed in the past--mimeographing--might be found. Accordingly, two informal investigations were made some time ago. Mr. Brimmer, Secretary of the Laboratory, investigated the

possibilities of photolithography; and Messrs. Ruedenberg and Brimmer made a survey of typewriting equipment which could prepare copy for photolithographic reproduction and handle with facility the variety of physical, chemical, and mathematical symbols used in the scientific texts. As a result of Mr. Brimmer's investigation of lithoprinting, it has seemed practical and economically feasible to adopt the method of photolithography for reproduction of TECHNICAL REPORTS--not to mention the vastly improved appearance and legibility to be expected from this method. The recommendations of Messrs. Ruedenberg and Brimmer concerning their survey of typewriting equipment were that an International Business Machines Corporation electric typewriter of special design equipped with interchangeable typebars and various other features which would be extremely useful, be procured. The Department of Physics accordingly ordered such a machine, and delivery was made in February, 1953.

This electric typewriter is of rather unusual and special design. It is equipped with seventeen interchangeable key positions, into which 61 (or more) extra typebars may be used, thus providing an extraordinary variety (to wit, 126 symbols in addition to the usual 84 symbols) of scientific symbols to the otherwise limited possibilities of a standard keyboard. The design of the keyboard and the arrangement of the interchangeable typebars was the object of considerably study on the part of Messrs. Ruedenberg, Brimmer, and Roothaan, and of consultation with a representative of the IBM Corporation. As a result of the cooperation of the IBM Corporation and of the study made by these members of our group, the machine is so designed that it can accommodate virtually all textual material in the field of Chemical Physics.

It seems appropriate to acknowledge the efforts of those who brought about these innovations. We are indebted to Mr. C. H. Skinner, Manager of the Electric Typewriter Division of the International Business Machines Corporation of Chicago, who cheerfully undertook to provide this most unusual machine. We are indebted to Mr. Ralph Regalbuto, Practical Physicist of the Department of Physics, for the installation of the machine and for his designing, with Dr. Ruedenberg, and his construction of an ingenious rack to contain the interchangeable typebars. The Laboratory is indebted to Messrs. Ruedenberg, Brimmer, and Roothaan whose investigations and study made these improvements possible. In addition, Mr. Brimmer serves as administrative editor of these Reports. We are grateful to Mr. C. W. Scherr of this Laboratory for his draughting assistance. The enthusiastic cooperation of Mrs. Eugenia Bautista and Mr. William A. Lester, Jr., who have typed most of the lithoprint copy of this Report, in devising and learning wholly new techniques, is gratefully acknowledged.

3. Spectroscopic Apparatus and Equipment

For an account of the general program and of previously available equipment, reference may be made to the Report for the period 1 September 1948 to 31 May 1949, Part One.

The Harrison 21-foot vacuum grating spectrograph has been modified in a number of respects. A 30,000-lines-per-inch aluminized glass grating has been obtained from Bausch and Lomb and mounted in the instrument. Grating movement and rotation controls have been installed to make possible reproducible focus and wavelength settings. With these controls, the instrument has been focused from 500Å to 5,200Å in the first order.

making possible rapid shifts of spectral regions and spectral orders. The vacuum pumping system has been completely overhauled and a new Distillation Products Corporation MCF700 diffusion pump has been installed. Considerable improvement in ultimate vacuum and pumping speed have been obtained; it is now possible to pump the 750 liter volume to a pressure of somewhat less than one micron in 30 minutes.

Photographs of oxygen, carbon dioxide, ethylene, and deuteroethylene have been obtained in the first order from 1,600Å to 2,100Å. The resolving power at 1,800Å is about 60,000, which is one third the theoretical resolving power of the grating. In an effort to improve further the resolving power, a new precision spectroscopic slit is being constructed. This is a bilateral slit, will be adjustable from outside the instrument, and will carry a movable diaphragm in front of the slit.

Considerable effort has been applied toward spectroscopic light-source development. This work has resulted in a 1½-kilowatt hydrogen discharge tube which produces a rather intense continuum, and a hollow cathode arc which can be used to excite atomic emission lines of copper and iron.

Power supply development has paralleled the construction of discharge tubes. A 2,000-volt, 1½-ampere AC power supply, and a 2,000-volt, 1-ampere DC power supply, both with automatic switches, have been constructed and have proved very useful in exciting the discharge tubes.

A vacuum distillation system has been constructed which permits the high-vacuum distillation of low-boiling-point gases. Four different preparations and purifications of ethylene and one of carbon dioxide have been made in this system.

A vacuum double monochromator, designed by Professor John R. Platt and built in the shops of the Institute of Nuclear Studies, has been installed. The optical system is of fluorite and is intended for the 1,300-3,000Å region. Certain special features include quick conversion from a monochromator to a single-path spectrograph, a beam chopper to be used with the monochromator attachment, and a photomultiplier assembly and power supply to be used for photoelectric recording of light intensity. The photomultiplier amplifier system is low frequency AC and is coupled with the frequency of the chopped beam, thus eliminating a large part of the scattered light. This instrument is being tested and completed for use on experimental problems.

The Laboratory possesses a 1927 Steinheil spectrograph, with an aperture of 95mm in diameter, which has recently been returned to service. It has a set of interchangeable quartz and glass optics of varying focal lengths, allowing choice of high dispersion or high speed. At present, it is set up with f = 195mm, giving a speed of f:3, which is advantageous for studying low-intensity phosphorescence emission.

The low-temperature Dewar constructed by Mr. Potts has been modified by Mr. Ham to be used at temperatures intermediate between liquid nitrogen and room temperature.

The construction of a high-pressure bomb has been completed by Professor A. W. Lawson's high-pressure laboratory in the Institute for the Study of Metals, and is now being tested as to spectral range and efficiency.

4. Summary of Papers in Present Report

Paper 1 reports a new study of the Miescher-Baer emission bands. The bands were observed on the 84-cm normal-incidence vacuum spectrograph, and the measurements were

extended toward considerably shorter wavelengths than in the original work of Miescher and Baer. The analysis of the bands, and the experimental conditions under which the bands were produced, indicate that the system belongs to the NO^+ ion.

Paper 4 reports a similar study of the N_2^+ $(C \rightarrow X)$ bands, observed with the same apparatus, and also extended toward much shorter wavelengths. Some experimental evidence was found for inverse predissociation at the $v' = 3$ vibrational level.

In Paper 3, a Beckman run of the 2,500Å bands of benzene at low temperature yields experimental evidence for a $^3E_{1u}$ excited state, which had been predicted by MO calculations, but is ordinarily not observed because of the overlapping of the well known $^1B_{2u}$ state.

Apparatus and experimental methods for low-temperature (liquid-nitrogen) vacuum spectroscopy (down to 1,670Å) are discussed in Paper 11. The spectrograph used is a Carlo-Schmitt-Ott vacuum fluorite spectrograph.

In Paper 10 Professor Platt proposes a classification of the spectra of conjugated systems. This classification is based upon experimentally distinguishable features of spectral transitions; the author proposes that such a classification should be the basis upon which a theory is to be built.

In Papers 5, 6, 7, and 8, Messrs. Platt, Ruedenberg, and Scherr extend the theory and applications of the free-electron model for conjugated systems. Paper 5 gives the general theory; Paper 6 gives numerical calculations on a great number of condensed ring systems and related compounds; in Paper 7 a wire model is discussed which enables one to measure electron densities and bond orders; and Paper 8 is an investigation of the relationships between bond order and bond lengths.

In Paper 2, Dr. Löwdin gives improved approximate formulas for many-center integrals.

Paper 9 corrects an error in one of the formulas for the two-center Coulomb integrals, as reported earlier in this Report.

5. Work in Progress

Work with the 21-foot and 84-cm vacuum grating spectrographs is being continued by Dr. Wilkinson. Of particular interest is the study of the spectra of ethylene (C_2H_4) and the completely deuterated compound (C_2D_4). Another important subject in this area which is now being pursued is the investigation of the possibility of using the xenon and krypton continua as light sources.

Studies of the ultraviolet absorption spectra of pyridine and related compounds in solution are being pursued by Dr. Reid. Dr. Reid is also continuing the investigation of the visible and ultraviolet emission spectra of the carbonium ion, and has nearly completed his work on the pyridine-iodine molecular complex. Another study on molecular complexes, which is being carried out by Dr. Reid and Mr. Lichten, is the investigation of triplet-triplet transitions of the system benzaldehyde-naphthalene. Mr. J. S. Ham is also continuing his investigation of molecular complexes, notably complexes of iodine with heavily substituted benzenes at liquid-nitrogen temperatures.

The evaluation of the two-center Coulomb integrals, which is being carried out under a subcontract with the IBM Unit at Iowa State College, is nearly completed; about half of the results have been received, and the remainder is expected to follow

shortly. Pilot calculations on the auxiliary functions for the two-center Exchange integrals are continuing under Messrs. Ruedenberg, Kinyon, and Jaunzemis. The manuscript containing the analysis of the Hybrid integrals has been completed by Messrs. Ruedenberg, Roothaan, and Jaunzemis, and will be included in Part Two of this Report.

The computations on the first-row atoms have been taken over by Mrs. Gudrun Lenkensdorf and are progressing steadily. Studies on the free-electron model for conjugated systems are being continued by Messrs. Ruedenberg and Scherr. A program to carry out the calculations of a diatomic molecule with complete configuration interaction on an electronic digital computer is being worked out by Mr. Scherr.

6. Associated Activities

Work on the large-scale numerical evaluation and tabulation of the two-center Exchange integrals is being continued by Messrs. Ruedenberg, Roothaan, Merryman, and Jaunzemis under contract with the Office of Scientific Research (Air Research and Development Command). The planning for putting this problem on an electronic digital computer is progressing steadily. Predoctoral students N. S. Ham and A. D. McLean (both from the Department of Chemistry) are carrying on calculations on benzene and diatomic molecules, respectively. The study of Li_2 by J. E. Faulkner has been interrupted temporarily since his departure to the Oak Ridge National Laboratory, but is expected to be resumed at some time in the future. The study of N_2 by Mr. Scherr is continuing steadily (see also "Work in Progress" above).

TECHNICAL PAPERS